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Development of Chemically and Thermally  
Robust Lithium Fast Ion Conducting  
Chalcogenide Glasses

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## 1. Abstract

In this project, a new research thrust into the development of an entirely new class of FIC glasses has begun that may lead to a new set of optimized thin-film lithium ion conducting materials. New chemically robust FIC glasses are being prepared that are expected to exhibit unusually high chemical and electrochemical stability. New thermally robust FIC glasses are being prepared that exhibit softening points in excess of 500°C which will dramatically expand the usable operating temperature range of batteries, fuel-cells, and sensors using such electrolytes. Glasses are being explored in the general compositional series  $x\text{Li}_2\text{S} + y\text{Ga}_2\text{S}_3 + (1-x-y)\text{GeS}_2$ .  $\text{Li}_2\text{S}$  is added as the source of the conductive lithium ions.  $\text{GeS}_2$  is the base glassforming phase and the trivalent sulfides,  $\text{Ga}_2\text{S}_3$ , is added to increase the “refractoriness” of the glass, that is to significantly increase the softening point of the glass as well as its chemical stability. By optimizing the composition of the glass, new glasses and glass-ceramic FIC materials have been prepared with softening points in excess of 500°C and conductivities above  $10^{-3} (\Omega\text{cm})^{-1}$  at room temperature. These latter attributes are currently not available in any FIC glasses to date.

## 2. Introduction

Fast ion conducting (FIC) glasses have been known for some time since the discovery by Levasseur et al.<sup>1,2,3,4</sup>, Malugani et al.<sup>5,6</sup>, and Menetrier et al.<sup>7,8,9</sup> of alkali ion conducting chalcogenide glasses, by the former, and of silver ion conducting oxide glasses, by the latter two investigators. A nearly 100,000-fold increase in the ionic conductivity for a lithium ion conducting sulfide-based glass compared to its oxide analogue has been observed. Additionally, a further dramatic increase in the ionic conductivity for these ionically glasses can be achieved when a dopant salt like  $\text{LiI}$  is added to a base silver ion conducting glass.

However, the success that these lithium and silver ion conducting sulfide glasses have provided in increasing the ionic conductivity has come at a significant cost in the overall performance of these glasses. The very chemistry that produces the high ionic conductivities also produces glasses with softening points rarely in excess of 100° C and that are extremely, often violently, reactive with atmospheric moisture and oxygen. Such glasses offer little hope of ever

being commercially viable electrolytes in battery, fuel cells, and sensor systems due to their thermal and chemical instability.

It is to this great problem the current project is directed. New research will be proposed that is the result of the PI's more than 20 years experience in the study and development of FIC glasses. First, using a new and unique sulfide chemistry based upon a set of chemically stable sulfide glass formers, a new set of chemically stable and high ionic conductivity sulfide glasses will be developed for the first time. Second, combining this set of chemically stable chalcogenide glasses with a new set of refractory sulfide glassforming intermediates, a new class of thermally robust FIC glasses with softening points in excess of 500°C will be developed for the first time

### **3. Report of Progress on the Grant**

#### ***a. Selection of the Glass Forming Systems***

Glasses were proposed for study in the general compositional series  $x\text{LiI} + y\text{Li}_2\text{S} + z(\text{Ba}, \text{Zn}, \text{Sr})\text{S} + w(\text{Ga}, \text{La}, \text{Al})_2\text{S}_3 + (1-x-y-z-w)[m\text{GeS}_2:q\text{As}_2\text{S}_3:n\text{B}_2\text{S}_3:p\text{SiS}_2]$ . LiI and  $\text{Li}_2\text{S}$  are added as the source of the conductive lithium ions.  $\text{GeS}_2$ ,  $\text{As}_2\text{S}_3$ ,  $\text{B}_2\text{S}_3$ , and  $\text{SiS}_2$  are added, typically in mixtures of two or more, as the base glassforming phase. Finally, alkaline earth sulfides and trivalent sulfides, again in mixtures, are added to increase the "refractoriness" of the glass, that are expected to significantly increase the softening point of the glass as well as its chemical stability. The simplest of these compositions,  $\text{Li}_2\text{S} + \text{Ga}_2\text{S}_3 + \text{GeS}_2$ , was targeted for exploration first since the Li/Ge system is known to be a strong glass forming series with high  $\text{Li}^+$  ion conductivity and the binary Ga/Ge system is known to be a good glass forming series with very high glass transition temperatures combined with good chemical durability.

#### ***b. Development of Preparation Schemes for High Melting Point FIC Glasses***

A significant effort was expended to develop a preparation method that enabled these refractory chalcogenide materials to melted easily, reproducibly, and relatively cheaply at temperatures approaching 1,200°C. We have found from our previous work on related glasses that glassy carbon is an excellent material in which to melt these materials. However, it was quickly found that the lithium – thiogallogermanate phases could not be melted inside our glove box in our "crucible" melting system that moves crucibles from inside the glove box through an

airtight coupler and into a tube furnace connected to the side wall of the furnace. This system has an upper limit of 1,100°C and these compositions remained solids even after prolonged holding at these temperatures. It was found, however, that even with a crucible cover, the samples would volatilize and lose ~ 10 – 20 % of the charge.

Tall and thin vitreous carbon crucibles are filled with a three-gram batch of the starting materials, placed into the bottom of the silica tube that was then evacuated and sealed as shown in Fig. (1). The sealed tubes were placed into the furnace at 800°C and then ramped up to 950°C, held for 15-18 hours, and then ramped up again to 1100°C and held at temperature for 4 hours. The tubes were then dropped into a water bath to quench the sample to form a glass or slow cooled to form a polycrystalline ceramic.

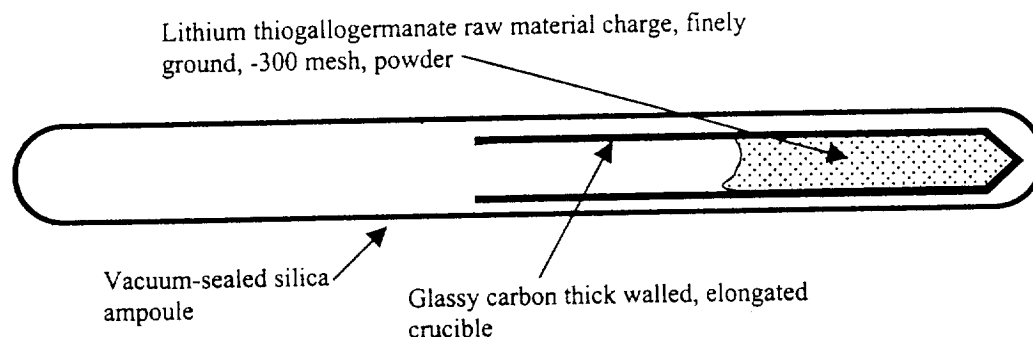


Figure (1) Typical reaction system used to melt and quench high T<sub>g</sub> glass and glass-ceramics materials. The charge is loaded into a glassy carbon crucible to protect it from oxide contamination from the silica ampoule. The carbon crucible charge is loaded inside a vacuum-sealed silica ampoule to protect the charge from volatilization and oxidation during melting. While the silica ampoule must be replaced for each preparation, the more expensive carbon crucible can be reused many times.

The silica tube showed small amounts of vaporization, but there was no evidence of corrosion of the silica. The carbon crucible also showed no signs of attack or corrosion from any of the materials. For most compositions, the resultant material, however, did not quench into a glass. The samples looked homogeneous, but also looked very refractory with no evidence of glass. The crystallization of the material could be due to the nature of the materials, in which case they are not glass formers, or it could be a slow quench rate due to the vacuum within the silica tube. The carbon crucible inside the silica does not make much contact with the silica and thus the thermal conductivity between the silica, which is cooled by the water, and the carbon

crucible is quite low. The low thermal conductivity may lead to a very slow quench rate thus allowing the materials to crystallize.

To achieve a purely glassy phase of these materials, the samples were re-melted inside our glove-box crucible melting system. Since the charge has been first reacted at elevated temperatures to achieve the equilibrium phases, the materials is now found to melt at a lower temperature,  $\sim 900^\circ\text{C}$  with little observed weight loss. The re-melting technique is done in an open crucible within a controlled atmosphere of the glove box.

### *c. Compositions Explored to Date*

The initial batch compositions were concentrated in the ternary diagram located near the  $\text{GeS}_2$  side of the diagram since the  $\text{GeS}_2$  is the major glass former of the system. The compositions that have been investigated are labeled 1-9 on the ternary diagram in Figure (1).

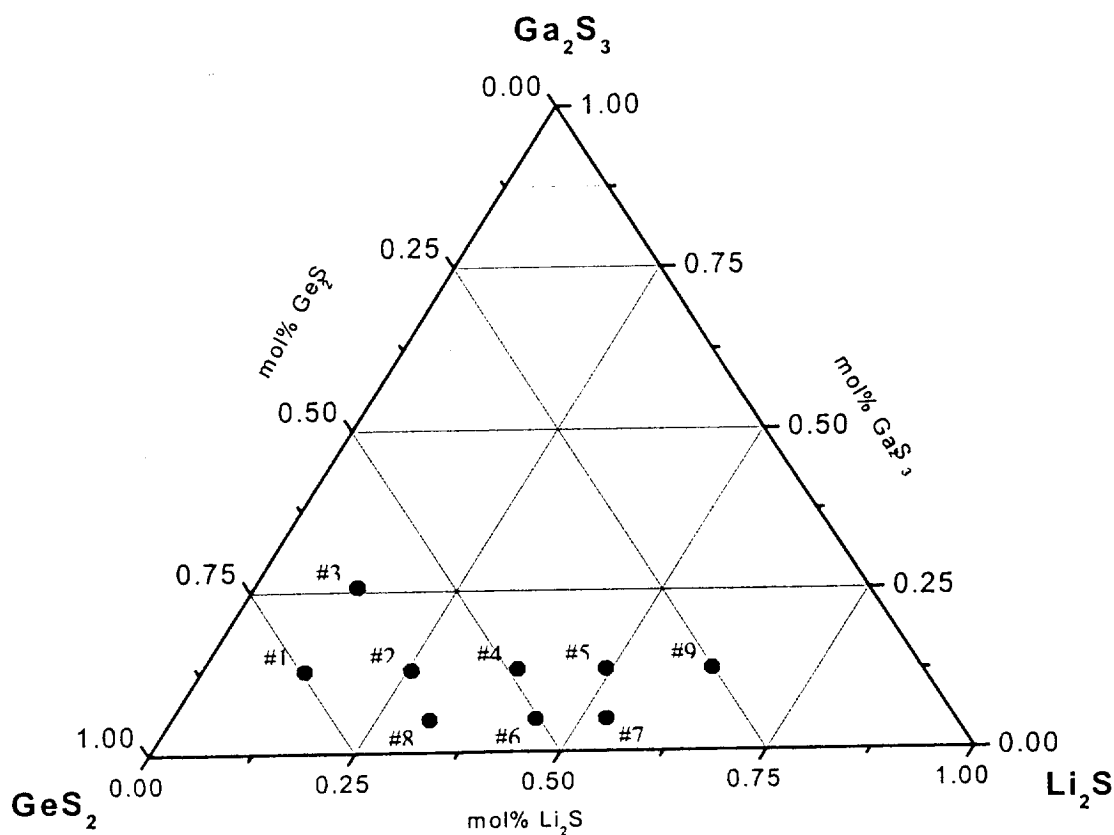


Figure 1. Ternary phase diagram of the  $\text{GeS}_2$  –  $\text{Ga}_2\text{S}_3$  –  $\text{Li}_2\text{S}$  compositions that have been investigated so far.

All of the investigated compositions shown in Figure (1) were initially melted in a carbon crucible sealed inside a silica tube and were observed to be homogeneous and crystalline. To obtain a sample size sufficient for conductivity measurements, all of these samples were re-melted inside a helium glove box. Composition #2 melted at 900°C and was poured out onto a brass plate, but did not form a glass. It remained visibly homogeneous and changed from a pale orange color to a dark red/orange color that was slightly glossy. Composition #8 was reheated to 1000°C and melted into a liquid, but it was too viscous to pour. Composition #8, although very viscous, could be pressed into a disc and thus had glassy properties, but upon cooling showed no visible signs of glass. In both cases, the weight loss was extremely low, about 0.4%, at all temperatures which shows that the GeS<sub>2</sub> has been incorporated into the material since it has the lowest sublimation temperature of 600°C. Composition #3 was also re-melted at 1000°C and could be poured out easily, but again did not show any visible signs of glass. The weight loss was about 7% for composition #3, but it is believed that it could be melted and poured at a much lower temperature than composition #2.

Significantly, all of the other compositions, 4, 5, 6, 7, and 9 had melting temperatures higher than the capabilities of the current furnace ~1150°C. This suggests that these compositions, *if they could be melted*, would yield glass and glass-ceramics that would be expected to have even higher melting temperatures than those of compositions 2, 3 and 8. While this result is frustrating in that these formed compositions cannot be melted, it is a positive indication that these compositions are indeed the appropriate ones to be investigating to develop high transition temperature FIC materials. We will spend some effort using even more sophisticated melting procedures to determine if these compositions can be melted or not.

#### ***d. Conductivity Measurements of the FIC Materials***

Using the re-melting technique, conductivity samples could be prepared from these samples and so far, one full temperature run of the conductivity has been made on one sample, composition #2, 0.25 Li<sub>2</sub>S + 0.125Ga<sub>2</sub>S<sub>3</sub> + 0.625GeS<sub>2</sub>. The sample was measured from 25 to 357°C, the current limits of the conductivity system we used. A newer system is being completed at this time which will enable conductivity runs to be completed from liquid N<sub>2</sub> temperatures, ~-160°C to 500°C.

The frequency dependence of the a.c. conductivity over this temperature range is shown in Fig. (2). The two ranges of behavior observed for this sample are the d.c. "plateau" of the conductivity, shown in the center region of the figure as the flat frequency independent conductivity and the electrode polarization region observed at higher temperatures and lower frequencies. The third region of the conductivity behavior, that of the a.c. frequency dependent conductivity, is not observed because for this particular sample over these particular temperatures and frequencies, the conductivity is so high such that the frequency is not able to exceed the condition  $2\pi f\tau \sim 1$ , where  $\tau$  is the so-called conductivity relaxation time describing some average hopping time of the ions in the glass. We will be able to observe this behavior in our new conductivity system where we can explore lower temperatures, hence longer  $\tau$ , and higher frequencies. However, we can at this time show that very high quality conductivity data can be obtained for these glasses and that the conductivities of these materials are quite high.

In Fig. (3), the d.c. conductivities are more accurately determined from the complex plane analysis of the complex impedance. A range of temperatures is presented to show a range of behaviors for the complex impedance.

Figure (4) shows the comparative behavior of the Arrhenius plots of the d.c. conductivity compared to those of related and comparable glasses and polycrystals. As can be seen, the lithium thiogallogermanate glass ceramic FIC materials are expected to yield the highest conductivities among these materials due to their high conductivity combined with their high melting points. This is quite impressive because this particular material only has 25 mole %  $\text{Li}_2\text{S}$  doping compared to the other materials that are in excess of 50 mole %  $\text{Li}_2\text{O}$ ,  $\text{Ag}_2\text{O}$ , or  $\text{Ag}_2\text{S}$ . Even more impressive is the fact that this particular glass-ceramic has not been doped with  $\text{LiI}$ , which is known to increase the conductivity as much as 2 to 3 orders of magnitude. Such doped materials are being prepared and will be reported on shortly.

#### **4. Summary and Research Plans for Second Year of the grant**

The first year of this grant has enable the personnel to be hired, the equipment to be assembled, proof of concept materials to be synthesized, characterized, and tested as well some preliminary results to be obtained that show that a class of very highly conductive, very high temperature FIC materials can indeed be developed. In the second year of this grant, as provided by a no-cost extension allowed by NASA GRC, we plan the following research:



1. Complete the high temperature conductivity system so measurements can be made in excess of 500 °C and over the extended frequency range of 0.01 Hz to 10 MHz.
2. Fully characterize the temperature and frequency dependence of the conductivity of the samples so far prepared, compositions 2, 3, and 8.
3. Fully characterize the cyclic voltammetry of these compositions to determine their electrochemical redox potentials.
4. Fully characterize the structures, using IR and Raman spectroscopies, and their thermal properties using DSC and DTA techniques.
5. Determine the stability of these phases in air and water using a combination of simple wet chemistry techniques as well as active atmosphere TGA.
6. Develop melting techniques to melt compositions richer in  $\text{Li}_2\text{S}$ , such as compositions 4,5,6,7, and 9 on Fig. (1). If such compositions can be melted and quenched into samples, they will be fully characterized as described above.
7. Begin exploring and characterizing the composition series  $\text{Li}_2\text{S} + \text{Ga}_2\text{S}_3 + \text{La}_2\text{S}_3$ .

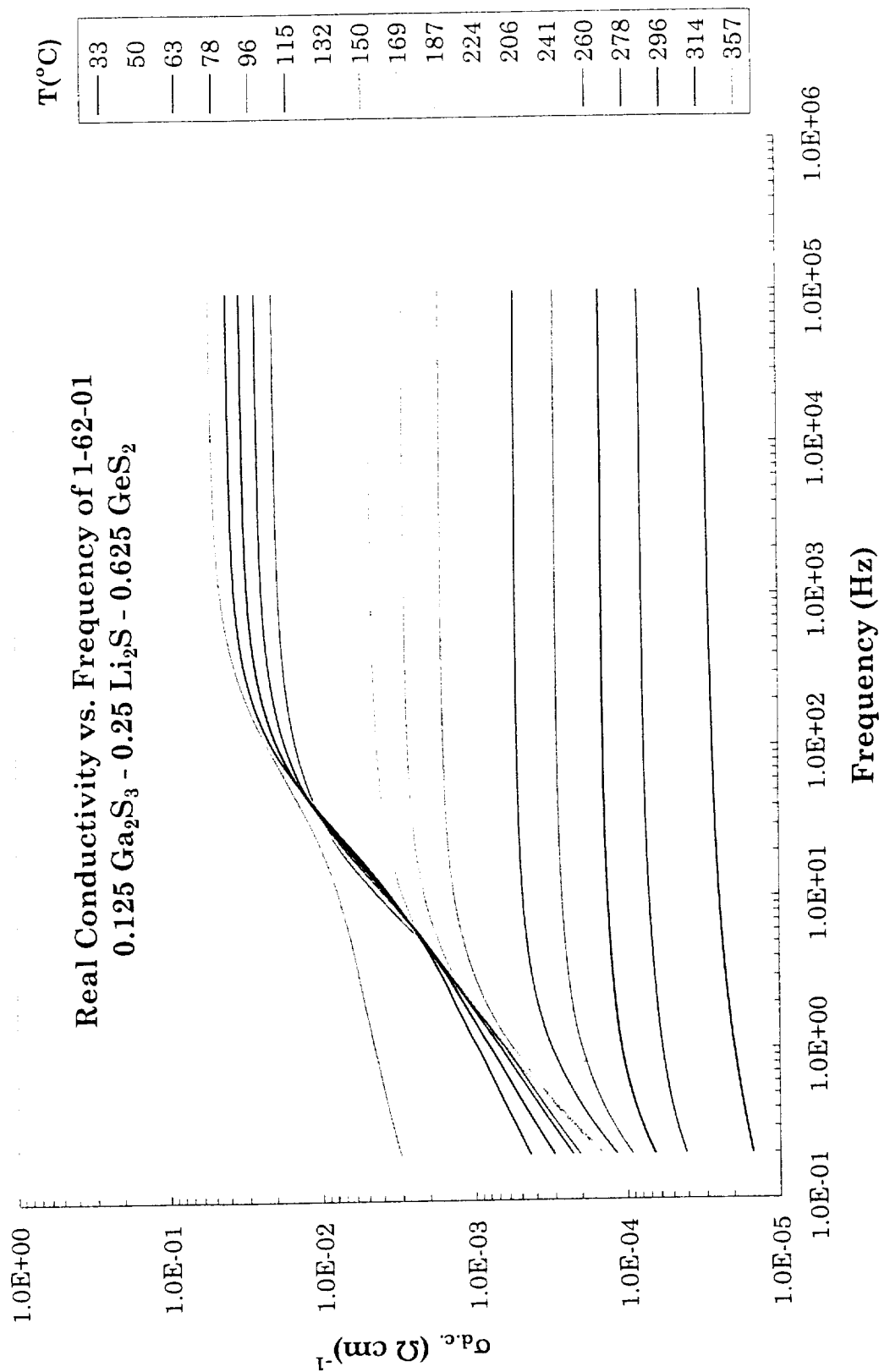


Figure (2) Frequency dependence of the d.c. conductivity for 0.25Li<sub>2</sub>S + 0.125Ga<sub>2</sub>S<sub>3</sub> + 0.625GeS<sub>2</sub> glass-ceramic from 33 to 357 °C. Thermal stability of the glass ceramic appears to be ~ 800°C. With such high conductivities, only the d.c. conductivity plateau and electrode polarization behaviors are observed. Measurements (in progress) below room temperature would be needed to see the typical frequency dispersion of the a.c. conductivity.

### Typical Complex plane plot for Li-Ga-Ge FIC Glass-Ceramic

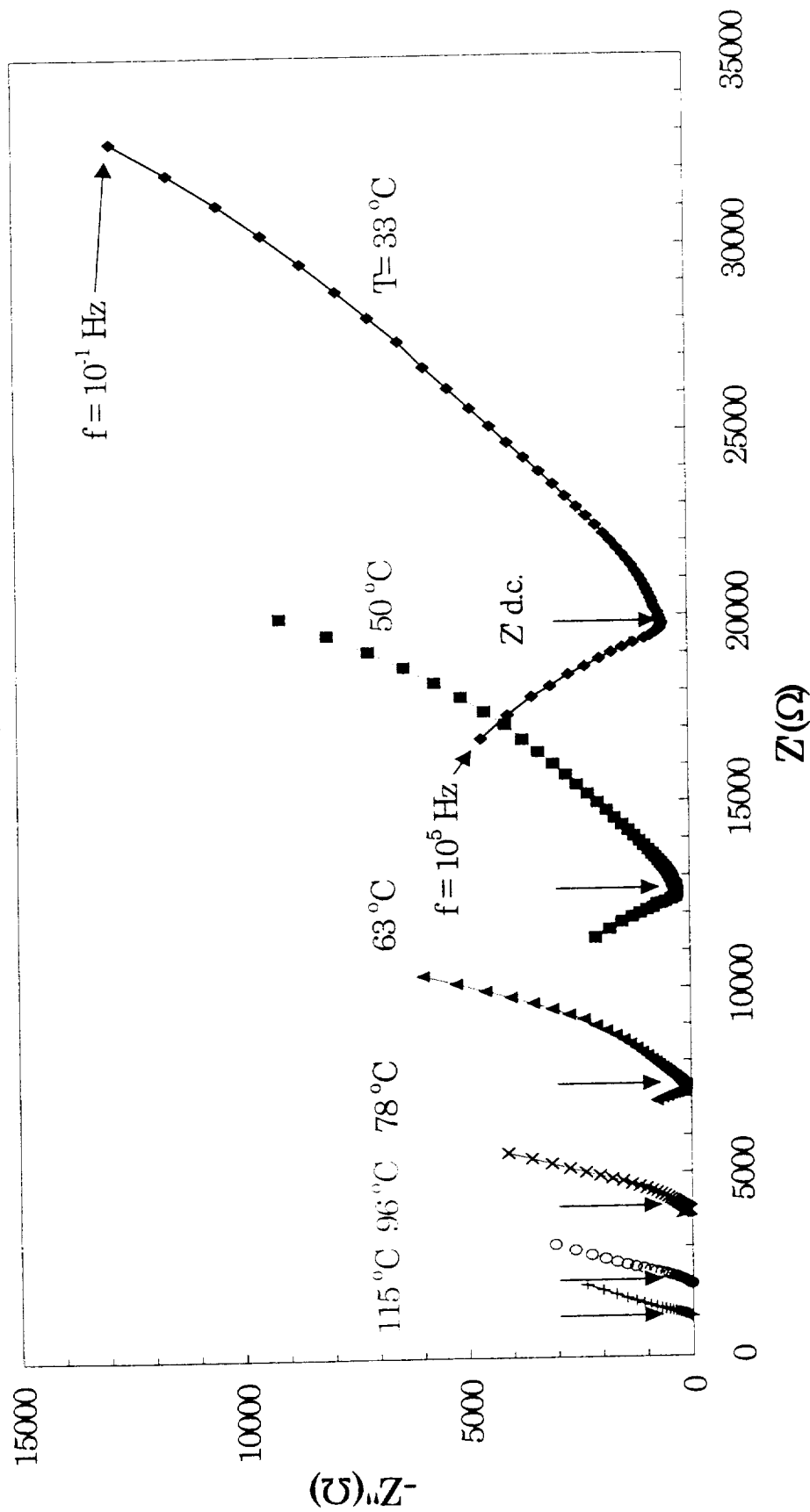


Figure (3) Typical complex plane impedance plots for the  $0.25 \text{ Li}_2\text{S} + 0.125 \text{ Ga}_2\text{S}_3 + 0.625 \text{ GeS}_2$  glass-ceramic over a range of relatively low temperatures. The d.c. conductivity is determined from these plots from the d.c part of the real impedance,  $Z'_{d.c.}$ , such points at each temperature are shown as arrows on the figure. The frequency range of each measurement sweeps from 0.1 Hz to 100 kHz and moves from the rightmost point to the leftmost point on each curve. Curves at higher temperatures are like those for 115 °C, single spikes that move to progressively lower impedances

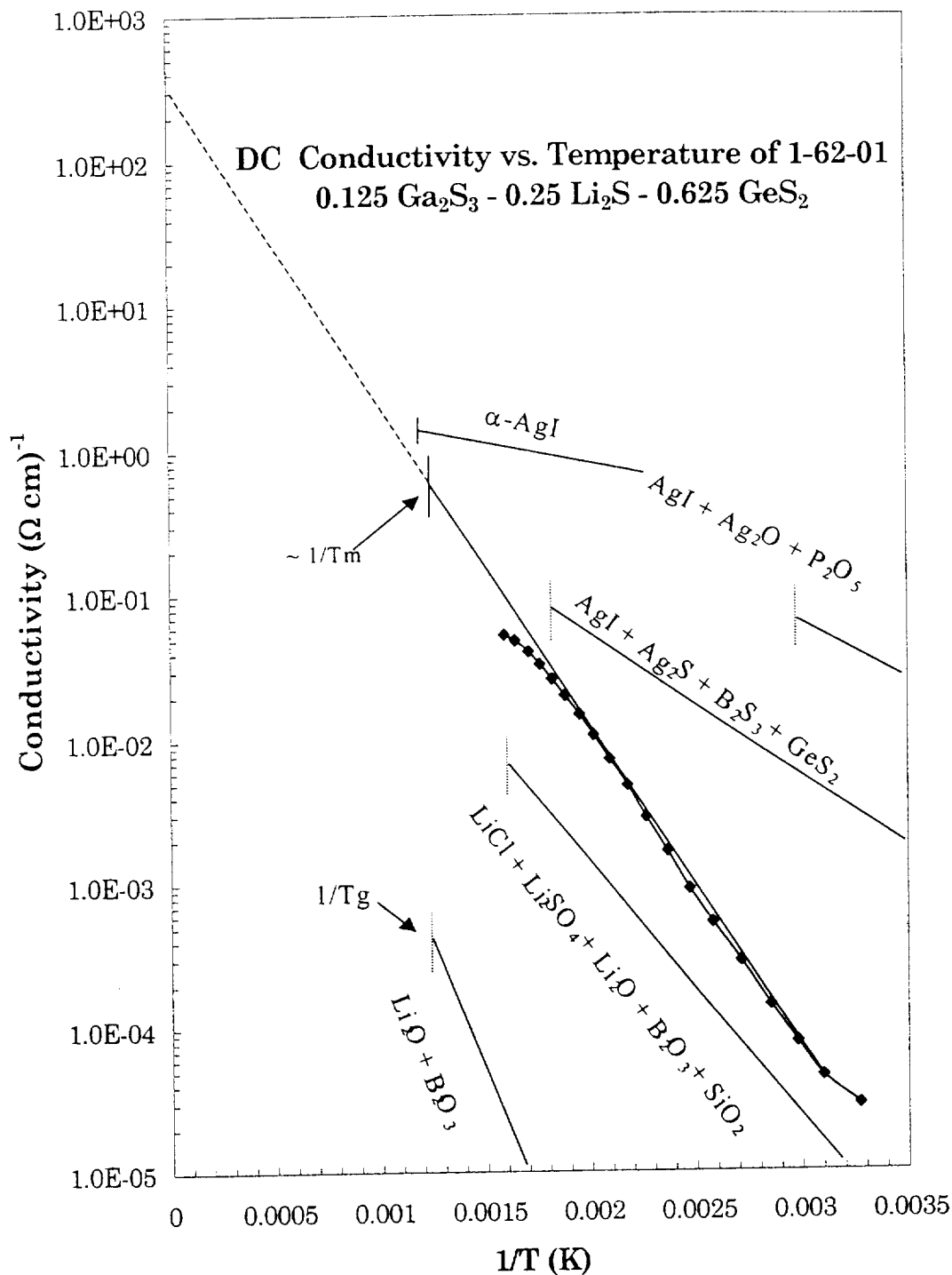


Figure (4). Arrhenius plots of the d.c. conductivities determined from Fig. (3) for the 0.25Li<sub>2</sub>S + 0.125 Ga<sub>2</sub>S<sub>3</sub> + 0.625GeS<sub>2</sub> glass-ceramic. Plotted for comparison are a poorly conducting oxide glasses, and optimized and higher conducting oxide glass as well as two silver chalcogenide FIC glasses. The high temperature conductivity of the FIC glass-ceramic is currently being examined to determine just how high the conductivity of this material can achieve at elevated temperatures. For comparison, the data for the best FIC material to date, α-AgI is plotted as well.

## 5. References

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